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(54) Process for the selective removal of hydrogen sulphide

(57) The selective removal of H_2S, COS, CS_2, and mercaptans from natural gases or synthesis gases also containing CO_2 is achieved by using an absorber solution containing specified tertiary amines and/or specified sterically hindered primary and/or secondary amines dissolved in organic solvent(s) and/or water, and mixing the gas leaving the absorber with regenerated absorber solution, then cooling the mixture formed, and finally separating the purified gas from the absorber solution which is fed to the top of the absorber.

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SPECIFICATION

Process for the selective removal of hydrogen sulphide

The present invention relates to a process for the selective removal of acidic gases from natural gases, or synthesis gases.

More particularly, the present invention relates to a process for the selective removal of H_2S and of other sulphur compounds (COS, CS_2, mercaptans, sulphides) from natural gases or synthesis gases, which contain also CO_2.

The problem of the selective removal of hydrogen sulphide and of other sulphur compounds (COS, CS_2, mercaptans) from natural gases or synthesis gases also containing CO_2 has been felt in the industry for a long time. Many situations exist in fact, in which it is desirable to remove as completely as possible the hydrogen sulphide, and other sulphur compounds, leaving most of CO_2 in the processed gas.

Here is a list of the most frequent cases:

—In the gas natural industry, specifications are in force, which are very restrictive (2–5 ppm) for H_2S, which is a poison, and are, on the contrary, rather wide (0.5–3%) for CO_2, which is an inert substance only.

When the content of CO_2 in the processed gas is low, it is expedient to remove H_2S only, with the CO_2 removal costs being saved.

—Some natural gases and some raw synthesis gases contain a small amount of H_2S and a large amount of CO_2, so that, by using a non-selective de-acidification process, the stream of separated acidic gases would contain, as a result, very diluted H_2S, generating problems in the downstream Claus unit for sulphur production. All this can be avoided by the adoption of a selective process.

—One of the methods for the purification of the off-gas from the Claus unit consists in the reduction of the residual sulphur compounds into H_2S, in the separation of H_2S from inerts and CO_2, and in the recycle of the concentrated H_2S stream to the Claus unit. In this case, a selective process is essential, otherways making CO_2 leave the system would not be possible.

The selective separation of hydrogen sulphide from carbon dioxide is a rather difficult problem, in as much as both of these components are, as such, and potentially acidic.

The process routes of the prior art consist of an absorption step and of a regeneration step. The raw gas is purified from H_2S and from the sulphur compounds in the absorption section, by washing by means of the regenerated solution. The rich solution exiting the absorpion section is regenerated by stripping with steam or with an inert gas in the regeneration section.

Whilst the regeneration section does not involve problems, the absorption section was found to pose some problems. In fact, the removal of the undesired compounds is accompanied by the evolution of heat, which heats the solution, decreasing the acidic load which can be achieved. The circulation of absorber solution results large.

It is known, even if scarcely practiced, that one of the means for decreasing the circulation of the absorber solution of the aminic plants, is that of cooling once, or more times, the absorber solution during the absorption, by drawing it from a suitable plate of the absorber tower, and reintroducing it, after cooling, to the immediately lower plate.

In case of a packed absorber tower, the constructive accomplishment of the cooling is more complex, in that for each cooling, it is necessary to insert in the tower a stack-plate, to be able to collect and draw the absorber solution. Very often, this complication, and the related cost are accepted, because many times the packed absorber tower results cheaper than the plate absorber tower.

We have found now that by using determined tertiary amines, and/or sterically hindered primary and/or secondary amines, according to the hereunder disclosed scheme, it is possible to solve the problem posed by the selective spearation of hydrogen sulphide, and/or of the other sulphur compounds (COS, CS_2, mercaptans) from carbon dioxide.

The solvents of the process according to the invention are tertiary amines and/or sterically hindered primary and/or secondary amines in solution in water and/or in an organic solvent.

The tertiary amines are selcted from those wherein the three hydrogen atoms of ammonia are substituted by alkyl or alkanol groups. The alkyl groups must have from one to four carbon atoms, arranged in either a linear or branched chain. The alkanol groups must have from two to five carbon atoms, they too in a linear or branched chain. The hydroxy functions of the alkanol groups must be not more than two, and may be bonded to any carbon atoms. At least one of the three groups must be an alkanol group.

The preferred tertiary amines are: methyldiethanolamine, dimethylethanolamine, thyldiethanolamine, diethylethanolamine, methyldiisopropylamine, diisopropylethanolamine, N,N–dimethyl –2–amino–2–methylpropan–1–ol, N,N–dimethyl–2–amino–2–methylbutan–1–ol, propyldiisopropanolamine, 2–dimethylamino–2–methyl–1,3–propanediol, 2–methyl–2–(methyl–β–hydroxyethylamino)–1–propanol, N,N–dimethyl–2–amino–propan–1– l.

Among the sterically hindered primary and secondary amines which can be advantageously used in the present invention, we remind the diamino-ethers, in which either one or both of the amino-groups can be also tertiary, as well as the amino-alcohols, which may possibly contain ether groups.

The preferred sterically hindered amines are: 1,2–bis–(tert–butylaminoethoxy)–ethane, 1–(pyrrolidinylethoxy)–2–(tert-butylaminoethyoxy)–ethane, tert–butylaminoethoxyethanol, 2–(2–tert–butylamino)–propoxyethanol, 2–(2–isopropylamino)–propoxyethanol, tert–amylaminoethoxyethanol, (1–methyl–1–ethylpropylamino)–ethoxyethanol, N–methyl–N–tert–butylaminoethoxyethanol, 2–(N–isopropyl–N–methylamino)–propoxyethanol, 3–aza–2,2,3–trimethyl–1,6–hexanediol, tert—butylaminoethanol, 2–tert–butylamino–1–propanol, 2–isopropylamino–1–propanol, (3–tert–butylamino)–n–butanol, 3–aza–2,2–dimethyl–1,6–hexanediol, 3–tertbutylamino–1–propanol, bis(tert—butylaminoethyl)–ether, 1,2–bis–(tert–butylaminoethoxy)–ethane, bis–(2–isopropylaminopropyl) –ether, 1,2–bis–(pyrrolidinylethoxy)ethane, 1,2–bis–(3–pyrrolidinyl–n–propoxy)–ethane, bis–(N–pyrrolidinylethyl)–ether, 1,2–bis–(pyperidinylethoxy)–ethane, 1–(pyrrolidinylethoxy)–2–(-tert–butylaminoethoxy)–ethane.

The amines can be used alone, or mixed with each other.

The organic solvent can be selected from N–methyl–3–morpholone, sulpholane, N–methyl–pyrrolidone, N–phenylmorpholine, N,N–dimethylimidazolydin–2–one, methanol, N–methyl–imidazole, n-butanol. These organic solvents can be used alone, or mixed with each other.

In the circulating solutions, the content of the constituents is preferably as follows:
—the amine, or the amines, in the proportion of from 20 to 96% by weight, more preferably of from 20 to 90% by weight, still more preferably of from 30 to 50% by weight;
—water, in the proportion of from 2 to 70% by weight, more preferably of from 4 to 22% by weight;
—the possible organic solvents, in such a proportion as to constitute the balance to 100%.

The process according to the invention comprises an absorption section, inside the absorber unit of which the sulphur compounds contained in the natural gas or in the synthesis gas are absorbed by means of an absorber solution, and a regeneration section, wherein the absorber solution is regenerated by means of stripping by steam or by an inert gas, in the regeneration unit.

The other basic characteristics of the present process consists in mixing the gas leaving the absorber unit with the regenerated solution, then cooling in a heat exchanger the so-formed mixture, and finally separating the purified gas from the absorber solution, which is fed to the top of the absorber tower.

The absorber tower can be of the plate-type, or of the packed-type: in fact, by such a refrigerator, also the advantage is achieved that the use of a packed absorber does not require the above mentioned constructive complications.

In order to obtain a good mixing of the absorber solution with the gas leaving the absorber tower top, the absorber solution can be nebulized before being introduced into the overhead gas stream, or the overhead gas stream can be intaken by means of an ejector, the drive fluid of which is constituted by the absorber solution, or, according to a further variant, by using a Venturi scrubber.

The subject process of the present invention is recommended in particular in case of selective removal of H_2S and of at least one further sulphur compound (COS, CS_2, mercaptans).

Some Examples are now given to the purpose of better illustrating the invention, which Examples are not to be regarded as being limitative of the same invention.

Examples 1–2

A raw gas, having the following composition:

H_2S	1.600% by volume
CO_2	12.500% by volume
CH_4	85.864% by volume
COS	0.017% by volume
CH_3SH	0.019% by volume
	100.000% by volume

available under th pressur of 63.8 kg/cm², and at the temperature of 21°C, and flowing at a flowrate of 19,289.5 kmol/h was treated according to the present proc ss: in Example 1, with an aqueous solution of tertiary amines; and in Example 2, with a prevailingly organic solution of tertiary amines, with in both of the Examples a refrigerator being used for refrigerating th regenerated solution mixed with the overhead gas absorber, plus a 7-theor tical-plate absorber, with the results as shown in Tabl 1 (wher in also the operating c nditions are reported) being obtained.

Examples 3–4 (Comparative Examples)

The same raw gas as specified above was treated: in Example 3, with the same aqueous solution of Example 1; and, in Example 4: with the same previalingly organic solution of tertiary amines of Example 2, with an 8-theoretical-plate absorber tower and two intercoolers being used, without the gas exiting the absorber unit being mixed with the regenerated absorber solution, with the results as reported in Table 1 being obtained.

From a reading of said Table, we can observe that, by adopting the process according to the present patent application, a descrease is obtained in the circulation stream of the absorber solution, with a consequent reduction in costs.

Table 1

Examples	*1*	*2*	*3*	*4*
—Absorber solution				
MDEA, % by weight	50	–	50	–
H_2O, % by weight	50	10	50	10
NMP, % by weight	–	50	–	50
DMEA, % by weight	–	40	–	40
—Treated gas				
H_2S, ppm by vol.	4	4	4	4
CO_2, % by vol.	5.4	9.8	5.5	9.4
COS, ppm by vol.	166	1	165	1
CH_3SH, ppm by vol	1	1	2	1
—Duties, MMKcal/h				
Pre-saturator	18.7	7.2	–	–
1st Intercooler	–	–	4.5	3.7
2nd Intercooler	–	–	8.5	1.6
Refrigerating gas	–	–	5.8	2.8
—Absorber bottom temp., °C	43	41	47	42
—Solution circulation, t/h	572	483	605	559
—Circulation decrease, %	5.45	13.6	–	–

wherein:
MDEA=Methyldiethanolamine,
NMP=N–methylpyrrolidone,
DMEA=Dimethylethanolamine.

CLAIMS

1. A process for the selective removal of a sulphur compound from a natural or synthesis gas which additionally contains carbon dioxide, in an apparatus comprising an absorption section in which the sulphur compound contained in the natural or synthesis gas is absorbed by means of an absorber solution and a regeneration section in which the absorber solution is regenerated; at least part of the gas leaving the absorption section being mixed with at least part of the regenerated solution and the resulting mixture then being separated, after being cooled, so that the purified gas and the absorber solution are obtained, at least part of the absorber solution being fed to the absorption section; and the absorber solution comprising:

(1) one or more amines selected from tertiary amines wherein the nitrogen atom is bonded to three groups, namely (a) an alkyl group, (b) an alkanol group, and (c) a (same or different) alkyl or alkanol group, the alkyl groups being linear or branched groups having from 1 to 4 carbon atoms, and the alkanol groups being linear or branched groups having from 2 to 5 carbon atoms and not more than two hydroxy groups bonded to any one of the carbon atoms, and/or from sterically hindered primary and/or secondary amines selected from diaminoethers and aminoalcohols the latter optionally containining one or more ether groups; and

(2) one or more organic solvents and/or water, said organic solvents being selected from compounds able to keep in solution, in one single liquid phase, both the amine or amines and water.

2. A process according to claim 1, wherein the tertiary amine is one or more of methyldiethanolamine; dimethylethanolamine; ethyldiethanolamine; diethylethanolamine; methyldiisopropylamine; diisopropylethanolamine; N,N–dimethyl–2–amino–2–methylpropan–1–ol; N,N–dimethyl–2–amino–2–methylbutan–1–ol; pr pyldiisopropanolamine; 2–dimethylamino–2–methyl–1,3–propanediol; 2–methyl–2–(methyl–β–hydroxyethylamino)–1–propanol; and N,N–dimethyl–2–amino-propan–1–ol.

3. A process according to claim 1 or 2, wh rein the st rically hindered amin is on or more of 1,2–bis–(tert–butylaminoethoxy)–ethane; 1–(pyrrolidinylethoxy)–2–(tert–butylaminoethoxy)–ethane; tert–butylaminoethoxyethanol; 2–(2–tert–butylamino)–propoxyethanol; 2–(2–isopropylami-

no)–propoxyethanol; tert–amylaminoethanoxyethanol; (1–methyl–1–ethylpropylamino)–ethoxyethanol; N–methyl–N–tert–butylaminoethoxyethanol; 2–(N–isopropyl–N–methylamino)–propoxyethanol; 3–aza–2,2,3–trimethyl–1,6–hexanediol; tert–butylaminethanol; 2–tert–butylamino–1–propanol; 2–iso–propylamino–1–propanol; (3–tert–butylamino)–n–butanol; 3–aza–2,2–dimethyl–1, 6–hexandiol; 3–tert–butylamino–1–propanol; bis(tert–butylaminoethyl)–ether; 1,2–bis–(tert–butylaminoethoxy)–ethane; bis–(2–isopropylaminopropyl)–ether; 1,2–bis–(pyrrolidinylethoxy)ethane; 1,2–bis–(3–pyrrolidinyl–n–propoxy)–ethane; bis–(N–pyrrolidinylethyl)–ether; 1,2–bis–(pyperidinylethoxy)–ethane; and 1–(pyrrolidinylethoxy)–2–(tert–butylaminoethoxy)–ethane.

4. A process according to any of claims 1 to 3, wherein the organic solvent is one or more of N–methyl–3–morpholone; sulpholane; N–methyl-pyrrolidone; N,N–dimethylimidazolydin–2–one; methanol; N–methylimidazole; and n–butanol.

5. A process according to any of claims 1 to 4, wherein the absorber solution comprises said amine or amines in an amount of from 20 to 90% by weight, water in an amount of from 2 to 70% by weight, and optionally said organic solvent or solvents forming the balance to 100% by weight.

6. A process according to claim 5, wherein the water is present in an amount of from 4 to 22% by weight.

7. A process according to any of claims 1 to 6, wherein the mixing of the gas leaving the absorption section with the regenerated solution is effected by nebulizing the regenerated solution before introducing it into a referigerator unit together with said gas.

8. A process according to claim 7, wherein the mixing is carried out by means of an ejector the drive fluid of which is the regenerated solution.

9. A process according to claim 7, wherein the mixing is carried out by means of a Venturi scrubber.

10. A process according to any of claims 1 to 9, wherein the absorber solution comprises at least one of said tertiary amines and at least one of said sterically hindered primary and/or secondary amines.

11. A process according to any of claims 1 to 10, wherein the absorber solution comprises said amine or amines in an amount of from 20 to 96% by weight.

12. A process according to any of claims 1 to 11, wherein said sulphur compound is H_2S, COS, CS_2 or a mercaptan.

13. A process according to claim 1, substantially as described in any of the Examples.

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